



Journal of Coordination Chemistry

ISSN: 0095-8972 (Print) 1029-0389 (Online) Journal homepage: https://www.tandfonline.com/loi/gcoo20

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To cite this article: Sibongile Pikoli, Eric Hosten & Abubak'r Abrahams (2020): The effect of ligand design on the structural and photophysical properties of Nd(III) complexes with Schiff bases of the [(phenylimino)methyl]phenol-type, Journal of Coordination Chemistry, DOI: 10.1080/00958972.2020.1750604

To link to this article: https://doi.org/10.1080/00958972.2020.1750604



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The effect of ligand design on the structural and photophysical properties of Nd(III) complexes with Schiff bases of the [(phenylimino)methyl]phenol-type

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ABSTRACT

Three mononuclear Nd(III) complexes [Nd(HL₁)₂(NO₃)₃] (**1**, HL₁=2methoxy-6-[(*E*)-(phenylimino)methyl]phenol), [Nd(HL₂)₃(NO₃)₃] (**2**, HL₂=5-methoxy-2-[(*E*)-(phenylimino)methyl]phenol) and [Nd(HL₃)₂ (NO₃)₃]·CH₃OH (**3**, HL₃=2-methoxy-6-{(*E*)-[(2-methoxyphenyl)imino]methyl}phenol) were prepared in a 1:3 ratio (M:L) in methanol. The effect of the ligand substituents and their positions (*meta versus para*) on the electronic and photophysical properties of the complexes is demonstrated. Single-crystal X-ray diffraction studies show that HL₁ and HL₃ coordinate bidentate *via* the phenolate and methoxy oxygens, while HL₂ is bound monodentately through the phenolate oxygen, with the coordination environment completed by three η^2 -chelated nitrates. The significant differences observed in the coordination chemistry of the three Nd(III) complexes provides the opportunity for biological application investigations.

ARTICLE HISTORY

Received 13 January 2020 Accepted 16 March 2020

KEYWORDS

Lanthanide(III); Schiff base; o-vanillin; crystal structure; geometry; photophysical



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Supplemental data for this article is available online at https://doi.org/10.1080/00958972.2020.1750604.

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Figure 1. Structures of the *o*-vanillin-derived Schiff base ligands (HL₁₋₃).

1. Introduction

Schiff base ligands and their Ln(III) complexes are of interest due to their biological activity which includes antitumor, antibacterial, antiviral and antimalarial [1–3]. These properties are enhanced upon complexation due to synergistic effects [4]. Other applications include catalysis, optical sensors and magnetism [5,6].

The synthesis of lanthanide-centered molecules which exhibit a broad range of chemical and physical properties is desirable [7,8]. The ligand environment significantly influences the stereochemistry of lanthanide molecular materials leading to higher activity in catalysis, biochemistry and spectroscopy [9–11]. Accordingly, ligand selection should be considered in the synthesis of multi-functional, lanthanide-based compounds. Schiff bases are preferred due to their ease of synthesis and various donor groups [12,13]. Their electronic and steric properties can be modified to control the chemistry of the complexes synthesised through the introduction, or the rearrangement, of suitable substituents [14–16].

Studies on *o*-vanillin-derived Schiff bases 2-methoxy-6-[(*E*)-(phenylimino)methyl]phenol (HL₁), 5-methoxy-2-[(*E*)-(phenylimino)methyl]phenol (HL₂) and 2-methoxy-6-{(*E*)-[(2-methoxyphenyl)imino]methyl}phenol (HL₃) revealed that they are potentially multidentate ligands with the ability to form stable coordination compounds with metal ions (Figure 1) [17–20]. These *o*-hydroxy Schiff bases can exist in two well-known tautomeric forms, *viz.* phenol-imine and keto-amine [21–24].

To contribute to the pool of Schiff base-derived compounds and their coordination chemistry with lanthanides by incorporating different substituents in the primary molecule has prompted the study of $[Nd(NO_3)_3 \cdot GH_2O]$ with HL₁₋₃. The aim of this study is

to show the effects of the ligand environment on the stereo- and electrochemistry of the compounds synthesized. The addition or removal of a substituent is expected to change the structural and photo-physical properties, and has the potential to expand the biological applications of lanthanide compounds with [(phenylimino)methyl]phenol-type ligands [25,26].

The steric and electronic effects of the ligand substituents on the bond parameters, the stereochemistry and the electrochemical properties were investigated using various *physico-chemical* methods, including melting point, microanalyses, IR, NMR and UV–Vis spectroscopy and X-ray crystallography.

2. Experimental

2.1. Chemicals

The neodymium nitrate salt [Nd(NO₃)₃·6H₂O], *o*-vanillin, 4-methoxysalicylaldehyde and *o*-anisidine were sourced from Sigma-Aldrich, while phenylamine was purchased from FLUKA and used without further purification. All solvents (methanol, DMF, diethyl ether and deuterated DMSO- d_6) were used as received, purchased from Merck, with the exception of DMF which was purchased from Sigma-Aldrich.

2.2. Physical measurements

Melting point analyses were determined using a Stuart® Melting point apparatus SMP30 with benzoic acid as the test standard. In addition, conductivity measurements were carried out at room temperature using a HANNA (HI) 2300 EC/TDS/NaCl meter. Microanalyses of carbon, hydrogen, nitrogen and sulfur were conducted on an Elementar Vario EL Cube CHNS analyser. Infrared radiation spectra of the Schiff base ligands and lanthanide complexes were obtained with a Bruker Tensor 27 FT-IR spectrophotometer, equipped with the Platinum ATR attachment—the collected data were analyzed using OPUS 6.5 software. ¹H NMR spectra were recorded at room temperature using a Bruker AvancellI 400 Nuclear Magnetic Resonance (NMR) spectrometer and the data acquisition was performed on TopSpin 3.2. Analysis of the spectra was done using ACD/Labs software. Absorption and emission spectroscopic measurements were carried out at room temperature. The former was recorded on a Perkin-Elmer Lambda 35 UV–Vis spectrophotometer with processing done via UV WinLab. Fluorescence studies were conducted using a Perkin–Elmer LS-45 Fluorescence spectrometer and the FL Winlab software was applied to evaluate the data. X-ray crystallography data was collected from a Bruker Kappa APEX II CCD diffractometer. The data reduction and cell refinement were done using the SAINT software package [27]. The crystal structures were solved and refined using SHELXS97 and SHELX97, respectively [28–30]. Molecular graphics were obtained through ORTEP-III and Mercury [31–33]. The coordination geometries of the lanthanide complexes were analyzed using SHAPE 2.1. This program is based on the algorithm defined by Pinsky and Avnir for the calculation of continuous shape measures (CShM) [34,35]. Polyhedral views were generated with VESTA. Electrochemical studies were done using C3 Cell Stand for Bas Epsilon Version 1.30.64 system comprised of three electrodes: a platinum working electrode, a



Figure 2. The synthetic routes for 1-3.

platinum auxiliary electrode and a pseudo silver/silver chloride Re-5 reference electrode. The redox behaviors of the lanthanide complexes were analyzed using 0.10 M tetrabutylammonium perchlorate (TBAP) as supporting electrolyte.

2.3. Preparation of HL₁₋₃ and its complexes

The ligands reported in this research were synthesized according to literature procedures described for related compounds [36–41]. Complexes **1–3** were prepared following the procedures illustrated in Figure 2.

2.3.1. Synthesis of 2-methoxy-6-[(E)-(phenylimino)methyl]phenol (HL₁)

o-Vanillin (7.62 g, 50 mmol) and phenylamine (4.65 g, 50 mmol) were dissolved in methanol (50 mL) and stirred at reflux for one hour. The solvent was removed under reduced pressure to yield an orange crystalline product which was filtered off and dried under vacuum. Yield: 92.0%, m.p.=82.4 °C. Anal. *Calcd.* for C₁₄H₁₃NO₂ (%): C, 73.98; H, 5.77; N, 6.17. Found: C, 74.66; H, 5.63; N, 6.05. UV–Vis (DMF, λ_{max} nm (ϵ , M⁻¹ cm⁻¹)): 270 (178580), 303 (87990), 331 (91670). IR (cm⁻¹): (C–H) 3077–2888(w), v(–OCH₃) 2836(w), v(C = N) 1612(s), v(C–C) 1584(m), v(C_{Ph}–O) 1195(s). ¹H NMR (DMSO- d_6 , δ ppm): 8.93 (s, 1H, –CH = N–), 7.46 (t, 3H, Ar), 7.41 (d, 2H, Ar), 7.32–7.23 (d, 1H, Ar), 7.12 (d, 1H, Ar), 6.91 (t, 1H, Ar), 3.81 (s, 3H, –OCH₃), 2.08 (s, 1H, –OH).

2.3.2. Synthesis of 5-methoxy-2-[(E)-(phenylimino)methyl]phenol (HL₂)

The Schiff base ligand HL₂ was prepared by stirring 4-methoxysalicylaldehyde (7.61 g, 50 mmol) and phenylamine (4.66 g, 50 mmol) in 50 mL methanol at reflux for 45 minutes. Removal of the solvent yielded a yellow solid which was dried overnight under vacuum. Yield: 87.4%, m.p.=86.4 °C. Anal. *Calcd.* for C₁₄H₁₃NO₂ (%): C, 73.98; H, 5.77; N, 6.17. Found: C, 74.16; H, 5.56; N, 5.98. UV–Vis (DMF, λ_{max} nm (ϵ , M⁻¹ cm⁻¹)): 285 (84810), 337 (156670). IR (cm⁻¹): v(C–H) 3075–2924(w), v(–OCH₃) 2840(w), v(C = N) 1584(s), v(C–C) 1564(m), v(C_{Ph}–O) 1189(s). ¹H NMR (DMSO-*d*₆, δ ppm): 13.68 (s, 1H, –OH), 8.87 (s, 1H, –CH = N–), 7.55 (d, 1H, Ar), 7.45 (d, 2H, Ar), 7.39 (d, 2H, Ar), 7.29 (t, 1H, Ar), 6.56 (t, 1H, Ar), 6.50 (t, 1H, Ar), 3.82 (s, 3H, –OCH₃).

2.3.3. Synthesis of 2-methoxy-6-{(*E*)-[(2-methoxyphenyl)imino]methyl}phenol (HL₃) HL₃ was synthesized by stirring a solution of o-vanillin (7.61 g, 50 mmol) and o-anisidine (6.16 g, 50.0 mmol) in 50 mL methanol at reflux for 60 min. The resulting yellow solution was concentrated using a rotary evaporator, and the yellow precipitate produced was dried under vacuum. Yield: 85.1%, m.p.=97.2 °C. Anal. *Calcd.* for C₁₅H₁₅NO₃ (%): C, 70.01; H, 5.88; N, 5.45. Found: C, 70.76; H, 5.87; N, 5.28. UV–Vis (DMF, λ_{max} nm (ϵ , M⁻¹ cm⁻¹)): 281 (62570), 313 (70760), 359 (28570). IR (cm⁻¹): v(C–H) 3035–2893(w), v(–OCH₃) 2838(w), v(C = N) 1613(s), v(C–C) 1588(m), v(C_{Ph}–O) 1179(s). ¹H NMR (DMSO-*d*₆, δ ppm): 14.08 (s, 1H, –OH), 8.96 (s, 1H, –CH = N–), 7.43 (d, 1H, Ar), 7.30 (t, 1H, Ar), 7.19–7.04 (t, 4H, Ar), 6.88 (t, 1H, Ar), 3.87–3.82 (s, 6H, –OCH₃).

2.3.4. Synthesis of [Nd(HL₁)₂(NO₃)₃], 1

A solution of HL₁ (0.1698 g, 0.7470 mmol) in 10 mL methanol was allowed to slowly diffuse into a solution of [Nd(NO₃)₃·6H₂O] (0.1102 g, 0.2514 mmol) in 10 mL methanol. Slow evaporation of the solvent over 2 days yielded orange crystals suitable for X-ray analysis. Yield: 50.6%, m.p.=222.9 °C. Anal. *Calcd.* for NdC₂₈H₂₆N₅O₁₃ (%): C, 42.84; H, 3.34; N, 8.93. Found: C, 42.43; H, 3.30; N, 9.06. Conductivity (10⁻³ M, DMF): 81.1 ohm⁻¹ cm² mol⁻¹. UV–Vis (DMF, λ_{max} nm (ϵ , M⁻¹cm⁻¹)): 273 (21340), 297 (25670), 339 (25840). IR (cm⁻¹): v(OH) 3035(w), v(C–H) 2943–2986(w), v(–OCH₃) 2831(w), v(C = N) 1633 (s), v(C–C) 1590 (s), v(C–O_{Ph}) 1172(s), v₄(NO₃⁻) 1453(s), v₁(NO₃⁻) 1287(s), v₂(NO₃⁻) 1028(m), v₅(NO₃⁻) 732(s), v(Nd–O) 486(s). ¹H NMR (DMSO-d₆, δ ppm): 13.23 (s, 2H, OH), 8.96 (s, 1H, –CH=N–), 7.48–7.33 (t, d, t, 5H, Ar), 7.24–6.94 (d, d, t, 3H, Ar), 3.83 (s, 3H, –OCH₃).

2.3.5. Synthesis of [Nd(HL₂)₃(NO₃)₃], 2

HL₂ (0.1701 g, 0.7484 mmol) was dissolved in 10 mL methanol and gradually added to a 10 mL methanolic solution of [Nd(NO₃)₃·6H₂O] (0.1099 g, 0.2507 mmol). The resultant mixture was refluxed for 45 min and subsequently filtered under reduced pressure. Diethyl ether was diffused into the solution at room temperature over 72 h, after which orange X-ray quality crystals were obtained and analysed. Yield: 31.6%, m.p.=208.8 °C. Anal. *Calcd*. for NdC₁₀₂H₉₁N₁₃O₃₆ (%): C, 55.19; H, 4.14; N, 8.21. Found: C, 54.34; H, 3.91; N, 8.30. Conductivity (10⁻³ M, DMF): 42.2 ohm⁻¹ cm² mol⁻¹. UV–Vis (DMF, λ_{max} nm (ϵ , M⁻¹ cm⁻¹)): 287 (87120), 337 (149100), 426 (6321). IR (cm⁻¹): v(OH) 3023(w), v(C–H) 3018–2942(w), v(–OCH₃) 2840(w), v(C = N) 1611(m), v(C–C) 1588 (s), v(C–O_{Ph}) 1164(s), v₄(NO₃⁻) 1453(s), v₁(NO₃⁻) 1281(s), v₂(NO₃⁻) 1024(m), v₅(NO₃⁻) 758(s), v(Nd–O) 463(m). ¹H NMR (DMSO-d₆, δ ppm): 13.67 (s, 2H, OH), 8.88 (s, 1H, –CH = N–), 7.56–7.39 (d, t, d, 5H, Ar), 7.28–6.50 (t, d, s, 3H, Ar), 3.82 (s, 3H, –OCH₃).

2.3.6. Synthesis of [Nd(HL₃)₂(NO₃)₃]·CH₃OH, 3

[Nd(NO₃)₃·6H₂O] (0.1089 g, 0.2484 mmol) was added to HL₃ (0.1938 g, 0.7497 mmol) in 20 mL methanol. After stirring at room temperature for 45 min, the solution was filtered under vacuum and isolated for 48 h to produce red-orange X-ray quality crystals. Yield: 35.2%, m.p.=228.4 °C. Anal. *Calcd.* for NdC₃₁H₃₄N₅O₁₆ (%): C, 42.46; H, 3.91; N, 7.99. Found: C, 42.04; H, 4.10; N, 8.05. Conductivity (10⁻³ M, DMF): 198.6 ohm⁻¹ cm² mol⁻¹. UV–Vis (DMF, λ_{max} nm (ϵ , M⁻¹ cm⁻¹)): 279 (67580), 313

6 👄 S. PIKOLI ET AL.

(76250), 362 (28330). IR (cm⁻¹): $v(OH)_{solvent}$ 3573(w), $v(OH)_{Ph}$ 3391(w), v(C-H) 3067–2950(w), $v(-OCH_3)$ 2845(w), v(C = N) 1631 (m), v(C-C) 1611 (m), $v(C-O_{Ph})$ 1165(s), $v_4(NO_3^-)$ 1451(s), $v_1(NO_3^-)$ 1224(s), $v_2(NO_3^-)$ 1028(m), $v_5(NO_3^-)$ 747(s), v(Nd-O) 427(w). ¹H NMR (DMSO- d_{6r} δ ppm): 14.07 (s, 2H, OH), 8.96 (s, 1H, -CH = N-), 7.44–7.30, 7.10 (d, t, q, 4H, Ar), 7.19, 7.04–6.88 (d, t, t, 3H, Ar), 3.87, 3.82 (s, 6H, $-OCH_3$).

3. Results and discussion

Complexes **1–3** are soluble in DMF and DMSO, partially soluble in ethanol, methanol and insoluble in diethyl ether and water. They are air-stable for months. The molar conductivity measurements in 10^{-3} M DMF reveal a 1:1 electrolytic nature for **1** (81.1 ohm⁻¹ cm² mol⁻¹), a 1:2 electrolyte for **3** (198.6 ohm⁻¹ cm² mol⁻¹) while the conductance of 42.2 ohm⁻¹ cm² mol⁻¹ (in **2**) suggests that considerable covalent interactions exist in the complex [11,42]. The formation of **1–3** is also confirmed by the agreement between the calculated and the experimental elemental analyses values.

3.1. Infrared spectroscopy

IR spectra of HL_{1-3} (Figure 3(a)) revealed a series of weak vibrations at 3080–2894 cm⁻¹ which can be assigned to the v(C-H) of the phenyl group, while the $v(O-CH_3)$ are found at 2836, 2840 and 2838 cm⁻¹ for HL_{1-3} , respectively. The vibrational frequencies attributed to the imine group in HL_{1-3} are detected at 1612, 1584 and 1613 cm⁻¹, respectively. The bands observed at 1195 cm⁻¹ (in HL_1), 1189 cm⁻¹ (in HL_2) and 1179 cm⁻¹ (in HL_3) are due to the $C-O_{Ph}$ vibrations [43].

For **1–3**, the phenyl C–H vibrations are shifted to $3067-2942 \text{ cm}^{-1}$ and the v(O-H) is observed at 3391 cm^{-1} (Figure 3(b)). The peak intensity of the phenolic frequency in **3** indicates the presence of intermolecular hydrogen bonding in the crystal lattice [44]. Additionally, a new broad peak appearing at 3573 cm^{-1} in the spectrum of **3** is attributed to the –OH stretch, and signals the presence of a crystalline –OH solvent in the coordination sphere [45]. The $v(C-O_{Ph})$ that is blue-shifted to 1172 cm^{-1} (for **1**), 1164 cm^{-1} (for **2**) and 1165 cm^{-1} (for **3**), and the appearance of the v(Nd-O) at 486, 463 and 427 cm^{-1} in **1–3**, respectively, reveal that the coordination of HL_{1–3} to the Nd(III) ion occurs *via* the phenolic and methoxide oxygen binding sites [46,47]. The minimal changes in the methoxy stretches of **1** and **3** (2831 and 2838 cm⁻¹, respectively) suggest weak interactions between the –OCH₃ group of the ligands and the metal center, while the absence of these changes in **2** indicates that coordination does not occur through the methoxide oxygen [48].

The azomethine stretching vibration is red-shifted to 1633 and 1611 cm^{-1} for **1** and **2**, respectively, and shifted to slightly lower frequencies for **3** at 1611 cm^{-1} . The peaks allocated in the regions $1611-1588 \text{ cm}^{-1}$ are assigned to the v(C-C) of **1–3**. The nitrates remain bound to the Nd(III) ions as demonstrated by stretching vibrations in the regions $1453-1451 (v_4)$, $1287-1224 (v_1)$, $1028-1024 (v_2)$ and $758-747 (v_5) \text{ cm}^{-1}$. According to the Lever separation rule, the separation of v_4 and v_1 (which is $\sim 200 \text{ cm}^{-1}$) signals covalent bidentate chelation of NO₃⁻⁻ in **1–3** [49].



Figure 3. (a) Overlay spectra of the *o*-vanillin-derived Schiff base ligands (HL_{1-3}). (b) The IR spectra of 1–3.

3.2. NMR spectroscopy

Selected ¹H NMR spectra of the free ligands and **1–3** in DMSO-*d*₆ are illustrated in Figures 4(a)–(d). The similar peak assignments of HL_{1–3} and **1–3** indicate that the ligand structure is maintained even after coordination to Nd(III). The hydroxyl peaks are shifted upfield from δ 13.30, 13.68 and 14.08 ppm in HL_{1–3} to δ 13.23, 13.24 and 14.07 ppm in **1–3**, respectively. These changes support the coordination of the ligands to the Nd(III) ion *via* the phenolic oxygen. The singlet at δ 8.93 ppm (in HL₁), δ 8.87 ppm (in HL₂) and δ 8.96 ppm (in HL₃) is assigned to the imino hydrogen. Upon coordination these peaks shift slightly to δ 8.96 and 8.88 ppm for **1** and **3**, respectively, whereas no changes are observed for **2**. The aromatic protons are detected as a series of multiplets in the range δ 7.56–6.50 ppm. The singlet at $\sim \delta$ 3.8 ppm is attributed to the methoxy hydrogens of the free ligands and the complexes [50,51].



Figure 4. (a) The ¹H NMR spectrum of the DMSO- d_6 solution of HL₁. (b). The proton NMR spectrum of HL₂ in DMSO- d_6 solvent at room temperature. (c). The ¹H NMR spectrum of the o-vanillin derived HL₃ ligand in DMSO- d_6 solvent. (d). An overlay of the spectra of the o-vanillin derived Schiff base free ligands HL_{1-3} and their complexes 1–3 in DMSO- d_6 solvent.

3.3. UV-Vis spectroscopy

UV-Vis spectra of the free ligands in DMF show three intra-ligand transitions, viz. 269, 302 and 332 nm (for HL₁), 291, 338 and 425 nm (for HL₂) and 280, 316 and 361 nm (for HL₃) which can be ascribed to $\pi \rightarrow \pi^*$ interactions of the benzene ring, and the $\pi \rightarrow \pi^*$ and the $n \rightarrow \pi^*$ transitions of the azomethine molety, respectively (Figure 5). The absorption properties of the conjugate organic ligands are determined by their chemical structure, the number of π -electron pair donating groups (such as –OH, –OCH₃, -CN and -NO₂) and their position [52].

8



Figure 4. Continued.

The *meta*-methoxy substituent on the phenol ring in HL_1 is excited at shorter wavelengths compared to the *para*-methoxy of HL_2 due to the significant conjugative effect in the *para*-position compared to the *meta*- and *ortho*-positions [53,54]. Moreover, the addition of the methoxy substituent on the second ring of HL_3 elongates the conjugate system which results in a small energy gap between the highest occupied molecular orbital (*HOMO*) and the lowest unoccupied molecular orbital (*LUMO*). Hence the intra-ligand transitions of the azomethine group and the phenolic ring in HL_3 occur at longer wavelengths compared to HL_1 [55].

After coordination, the $\pi \rightarrow \pi^*$ transition bands of the aromatic rings (273, 287 and 279 nm) and the imino bridge (297, 337 and 313 nm) are red-shifted for **1–3**, respectively (Figure 5). The $n \rightarrow \pi^*$ peaks of the > C=N-group are slightly blue-shifted to 339

10 👄 S. PIKOLI ET AL.



Figure 5. UV–Vis spectra of 10⁻³ M DMF solutions of HL₁, HL₂, HL₃ and 1–3.

(for 1), 426 (for 2) and 362 nm (for 3). These shifts are a result of the changes in the orbital energy levels of the free ligands upon complexation [56]. From the minimal energy shifts between the bands of the free ligands and those observed after coordination, it can be inferred that the ligand-to-ligand charge-transfer bands are not significantly influenced by coordination to the Nd(III) ion due to the Laporte forbidden $f \rightarrow f$ transitions [51,57]. The electronic data of the compounds synthesized are presented in Table 1.

3.4. Fluorescence spectra

The fluorescence measurements of the free ligands and **1–3** in DMF are displayed in Figures 6(a) and (b). The ligand substituents contribute significantly to the ability of the antenna to successfully transfer energy to the metal ion and enhance its emission intensity. This is dependent on the electron-withdrawing/-donating properties of the substituents [58]. The emission bands at 467, 531 and 574 nm with excitation wavelengths at 398, 531 and 573 nm are assigned to the ligand-centered transitions of HL_{1-3} , respectively. These bands are blue-shifted to 415 nm (for **1**), 527 nm (for **2**) and 533 nm (for **3**) excited at 293, 526 and 539 nm, respectively, confirming that complexation occurred (Table 2).

The metal-to-ligand charge-transfer (MLCT) band observed at 607 nm in **1**, from the triplet state of HL₁ to the lowest resonance energy level of the neodymium(III) ion $({}^{4}F_{3/2} \rightarrow {}^{4}I_{9/2})$, indicates HL₁ is an effective antenna to absorb and transfer energy to the lanthanide ion [59]. This is due to the electron-rich ligand environment and the chelate effect upon coordination [60]. For **2**, the *para*-methoxy substituent of HL₂ is sterically unfavorable, and therefore, coordination to the metal ion is not probable. This leads to fewer coordination sites, less electron-donation to Nd(III) and an ineffective shielding of the metal center from potential fluorescence quenching by the solvents. Thus, the Schiff base ligand in **2** is not a good antenna and the transition band

Compounds	λ _{max} (nm)	$\epsilon imes 10^4 \ (M^{-1} \ cm^{-1})$	Transitions
HL ₁	269; 302; 332	18.25; 8.80; 9.16	$\pi \rightarrow \pi^*$; $n \rightarrow \pi^*$
HL ₂	291; 338; 425	8.98; 15.66, 0.31	$\pi \rightarrow \pi^*; n \rightarrow \pi^*$
HL ₃	280; 316; 361	6.24; 7.01; 2.74	$\pi \rightarrow \pi^*; n \rightarrow \pi^*$
1	273; 297; 339	2.13; 2.57; 2.58	$\pi \rightarrow \pi^*; n \rightarrow \pi^*$
2	287; 337; 426	8.71; 14.91; 0.63	$\pi \rightarrow \pi^*; n \rightarrow \pi^*$
3	279; 313; 362	6.76; 7.63; 2.83	$\pi { ightarrow} \pi^*$; $n { ightarrow} \pi^*$

Table 1. Spectral data of HL₁₋₃ and 1–3.



Figure 6. An overlay of the fluorescence spectra of 10^{-3} M DMF solutions of HL₁, HL₂, HL₃, and 1, 2 and 3 at room temperature.

observed is ligand-centered [10,61]. The addition of another methoxy substituent to the second benzene ring of HL_3 is expected to increase the electron-donation toward the *f* metal due to a significant resonance effect. However, the dominating influence of the σ -withdrawing effect is displayed, and the *ortho*-OCH₃ group acts as an

12 👄 S. PIKOLI ET AL.

Compound	Excitation (nm)	Emission (nm)	Transition type
HL ₁	398	467	$\pi \rightarrow \pi^*$
HL ₂	526	531	$\pi { ightarrow} \pi^*$
HL ₃	573	574	$\pi { ightarrow} \pi^*$
1	293	415; 607	$\pi \rightarrow \pi^*$; ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$
2	526	527	$\pi \rightarrow \pi^*$
3	539	533	$\pi { ightarrow} \pi^*$

Table 2. Fluorescence data for HL_{1-3} and 1–3.

electron-withdrawing substituent (decrease in the energy transfer to the metal ion) [62,63]. Hence HL_3 is unable to effectively transfer energy to the *LUMO* of the Nd(III) ion.

3.5. Shape analysis

The coordination polyhedra of the Nd(III) complexes with HL_{1-3} are illustrated in Figures 7(a–c), with the CShM values listed in Table 3. The Nd(III) ions in **1** and **3** are ten-coordinate with the sphenocorona J87 ($C_{2\nu}$) and tetradecahedron (2:6:2) ($C_{2\nu}$) distorted geometries, respectively. The metal center in **2** is bound to nine oxygens in a muffin (C_s) geometry.

The distortion values are expected to decrease with decreasing coordination numbers consequential to steric requirements [64,65]. This is evidenced by the nine-coordinate complex **2**, and thus the least disorder being observed at 2.692. The coordination numbers for **1** and **3** are equal, however, a decrease in distortion is observed from 4.545 to 3.401, respectively. This anomaly can be ascribed to angular distortions (which are induced by small bite angles) that have more effect on the CShM values than bond lengths [66,67]. For **1**, the average bite angle between NO₃⁻ and the Nd(III) ion is 48.92°, while in **3** the average O_{nitrate}-Nd-O_{nitrate} bond angle is 49.97°, and thus more disorder exists. Additionally, the difference between the TD-10 and the JSPC-10 geometries in **3** is relatively small, which make the transitions between these two geometries more likely [66,68].

3.6. X-ray crystallography

Crystallographic data for **1–3** reveal diverse compositions due to the influence of the ligand environment. The three structures are mononuclear with the general formulas $[Nd(HL_1)_2(NO_3)_3]$, $[Nd(HL_2)_3(NO_3)_3]$ and $[Nd(HL_3)_2(NO_3)_3] \cdot CH_3OH$, as depicted by the *ORTEP* diagrams in Figures 8(a–c) for **1–3**, respectively.

The primary coordination sphere around Nd(III) in **1** is formed by two neutral bidentate *O*,*O*-donor HL₁ ligands and three η^2 -chelated NO₃⁻ anions that counter the 3+ charge of the metal center. The ten-coordinate structure crystallizes in the *P*bca space group and conforms to the spheronocorona geometry. HL₁ is coordinated to Nd(III) *via* the phenolate [Nd–O_{phenolate} bond lengths = 2.392(3) and 2.347(3) Å] and the methoxide oxygens [Nd–O_{methoxy} bond lengths are 2.747(3) and 2.614(3) Å]. The average Nd–O_{nitrate} bond distance is 2.561 Å.

In **2**, the metal center is bound by three monodentate HL_2 ligands and three η^2 -chelated NO_3^- anions, forming a nine-coordinate structure that has the muffin shape



Figure 7. (a). The polyhedral view of the sphenocorona coordination sphere of the ten-coordinate complex **1**. (b). The muffin (MFF) coordination polyhedron observed for the nine-coordinate Nd(III) complex **2**. (c). The tetradecahedron geometry of $[Nd(HL_3)_2(NO_3)_3]$ ·CH₃OH.

Shape	PPR, PAPR-10	JBCCU-10	JBCSAPR-10	JMBIC-10	JSPC-10	SDD-10	TD-10	HD-10
1	7.316	13.183	5.293	8.920	4.545	6.890	6.522	11.115
3	10.009	8.606	4.277	5.771	4.038	4.282	3.401	5.807
Shape	JCC-9	CCU-9	JCSAPR-9	CSAPR-9	JTCTPR-9	TCTPR-9	HH-9	MFF-9
2	9.220	7.930	3.910	2.973	3.752	3.459	10.603	2.692

Table 3. CShM values for 1–3.

geometry. The Nd–O_{phenolate} bond lengths are 2.379(13), 2.376(12) and 2.368(14) Å, with an average Nd–O_{nitrate} bond length of 2.553 Å.

The coordination mode of **3** is identical to that of **1**; two HL₃ ligands and three nitrate anions are bidentate to the Nd(III) ion, producing a neutral ten-coordinate complex. The Nd–O_{phenolate} and Nd–O_{methoxide} bond distances are 2.460(6), 2.391(6) Å and 2.656(7), 2.581(7) Å, respectively. The average Nd–O_{nitrate} bond distance is 2.543 Å. A solvent methanol has crystallized in the secondary coordination sphere, as indicated by the IR data.

The Nd–O bond distances of **1–3** are in accord with those previously reported for $[Nd(NCS)_3(HL_1)_3]$, with bond lengths ranging from 2.375(2) to 2.393(3) Å (for Nd–O_{phenolate}) and 2.742(3) to 2.843(3) Å) (for Nd–O_{methoxy}) [69]. Furthermore, the Nd–O_{nitrate} bond distances reported in **1–3** are comparable to the literature values of similar lanthanide *o*-vanillin-derived compounds [70].

In all three complexes HL_{1-3} remained protonated upon coordination to the metal ion. However, the phenolic proton migrated to the azomethine nitrogen, forming a phenolate anion which is more attracted towards Nd(III) [71]. The Nd–O_{phenolate} bond distances (average 2.388 Å) are notably shorter than the Nd–O_{methoxide} ones (average 2.650 Å), as a result of the more electron-rich phenolate oxygen after proton migration. For **2**, the methoxy substituent in the *para*-position results in monodentate coordination of HL₂, which is due to the energetically unfavorable steric constraints of this position. A correlation exists between the ligand substituents of HL_{1-3} and the bond distances between the neodymium(III) ion and the phenolate oxygen bond lengths from **1** to **3**. The addition of the *ortho*-OCH₃ group in **3** yields longer bond lengths between the phenolate oxygen donor-atoms and the Nd(III) ion as a result of the less electron-rich ligand environment compared to **1** and **2** [63,72].

The bond parameters of **1** and the neodymium compound reported by Z. Guoliang *et al.* are comparable [73]. The average Nd–O_{phenolate} and Nd–O_{methoxy} bond lengths for the latter are 2.373(3) Å and 2.843(3) Å, with an average Nd–O_{nitrate} bond length of 2.517 Å. In comparison to **1**, the inductive effect of the electron-donating *p*-methyl substituent is observed. Although the electron-releasing effect of the *p*-methyl carbon and its activation impact on the aromatic ring is small, it is evident in the more "electron-rich" neodymium ion [74,75]. Another consequence of the modification in the crystal structure can be seen with the space group which changes from monoclinic to orthorhombic upon removal of the *p*-methyl substituent.

The η^2 -chelated o-vanillin derivatives in **1** and **3** form a five-membered ring with an average bite angle of 62.03° and 62.27°, respectively (Table 4). The average nitrate bite angles were 48.92° (for **1**), 49.90° (for **2**) and 49.97° (for **3**). In relation to the shape measurements, the smaller bite angles result in higher deviations from the ideal geometry as a result of angular distortions, as evidenced in **1**. The bond angles of C11









Figure 8. (a). The *ORTEP* view of **1** showing 40% displacement ellipsoids and partial atom-labelling. (b). Molecular structure of **2**, with displacement ellipsoids drawn at 40% probability. The disordered molecules in the secondary lattice sphere were removed for clarity. (c). *ORTEP* perspective of **3** at 40% probability, with partial atom-labelling. Solvent ellipsoids were removed for clarity.

16 🕢 S. PIKOLI ET AL.

1		2		3	
Bond lengths (Å)		Bond lengths (Å) Bond leng		Bond lengt	hs (Å)
Nd1-011	2.392(3)	Nd1-011	2.379(13)	Nd1-011	2.460(6)
Nd1-012	2.747(3)	Nd1-021	2.376(12)	Nd1-012	2.656(7)
Nd1-021	2.347(3)	Nd1-031	2.369(14)	Nd1-021	2.391(6)
Nd1-022	2.614(3)	Nd1-041	2.554(16)	Nd1-022	2.581(7)
Nd1-031	2.521(4)	Nd1-042	2.536(17)	Nd1-031	2.511(7)
Nd1-032	2.531(3)	Nd1-051	2.528(16)	Nd1-032	2.575(7)
Nd1-041	2.506(3)	Nd1-052	2.531(17)	Nd1-041	2.526(7)
Nd1-042	2.648(3)	Nd1-061	2.608(14)	Nd1-042	2.562(7)
Nd1-051	2.576(3)	Nd1-062	2.559(16)	Nd1-051	2.554(7)
Nd1-052	2.581(3)			Nd1-052	2.527(10)
Bond angles (°)		Bond angles (°)		Bond angles (°)	
011-Nd1-012	60.94(9)	011-Nd1-021	159.36(5)	011-Nd1-012	60.9(2)
O21-Nd1-O22	63.11(10)	011-Nd1-031	90.49(5)	021-Nd1-022	63.63(19)
031-Nd1-032	49.54(12)	041-Nd1-042	50.11(5)	031-Nd1-032	50.0(2)
041-Nd1-042	48.82(10)	051-Nd1-052	50.58(5)	041-Nd1-042	49.8(2)
O51-Nd1-O52	48.40(10)	061-Nd1-062	49.02(5)	051-Nd1-052	50.1(3)
C11-N1-C121	128.9(4)	C11-N1-C121	126.54(16)	C11-N1-C121	127.9(8)

Table 4. Selected bond lengths (Å) and angles (°) in 1–3.

Table 5. Hydrogen bond parameters (Å, °) in 1–3.

$D - H \cdots A$	D-H	Н…А	DA	$D - H \cdots A$
		Complex 1		
N1 – H1…O11	0.78 (4)	1.6700	2.592(4)	143
N2 - H2…O21	0.80 (4)	1.94(4)	2.600(5)	139
C11 - H11…O42	0.9300	2.4900	3.414(5)	171.00
C12 - H12B…O21	0.9600	2.5400	3.157(5)	122.00
C126 - H126…O42	0.8800	1.9200	2.6215(19)	135.00
		Complex 2		
N1 – H1…O11	0.8800	2.0100	2.681(2)	133.00
N2 – H2…O21	0.8800	1.9300	2.631(2)	135.00
N3 — H3…O31	0.8800	1.9900	2.670(2)	134.00
N2 – H2…O61	0.8800	2.5100	3.198(2)	136.00
C12 – H12A…O53	0.9800	2.5600	3.532(3)	169.00
		Complex 3		
N1 – H1…O11	0.8800	1.9400	2.650(10)	136.00
N1 – H1…013	0.8800	2.2000	2.594(11)	106.00
N2 - H2…O21	0.8800	1.9800	2.668(10)	134.00
C11 – H11…O53	0.9500	2.5700	3.503(15)	167.00
C13 - H13A…O42	0.9800	2.4700	3.109(13)	122.00

D=donor, A=acceptor; symmetry codes: b = 2 - x, 1 - y, 1 - z (1); a = -1 + x, y, z (2); a = -1 + x, y, z (3).

and C121 surrounding the sp^2 hybridized azomethine nitrogen are 128.90(4)°, 126.54(16)° and 127.90(8)°, respectively, with a slight deviation from the ideal C–N–C angles of 120°.

Complex 2 contains a solvent molecule disordered around an inversion point and a coordinated nitrate with positional disorder. There is also a solvent void of 168 Å³ containing 62 electrons and a number of disordered methanol molecules were modelled in this void. For **3**, a methanol molecule with large anisotropic displacement parameters indicates disorder is observed. The hydrogens of methanol molecules in both **2** and **3** could not be located on the difference Fourier map or placed in calculated positions.



(a)





Figure 9. (a) Hydrogen bonding network in 1, (b) Unit cell structure of $[Nd(HL_2)_3(NO_3)_3]$, (c). Crystal packing illustrating the hydrogen bonding in 3.

18 🕒 S. PIKOLI ET AL.

Compound	1	2	3
Moiety formula	$C_{28}H_{26}N_5NdO_{13}$	2(C ₄₂ H ₃₉ N ₆ NdO ₁₅), C ₁₄ H ₁₃ NO ₂ , 3.988(CO)	$C_{30}H_{30}N_5NdO_{15}$, CO
$M_{\rm r}$ (g mol ⁻¹)	784.78	2363.02	872.84
Crystal system	Orthorhombic	Triclinic	Monoclinic
Space group	<i>P</i> bca	<i>P</i> -1	P2 ₁ /c
a, b, c (Å)	9.8282(3),	12.5752(5),	9.8234(6),
	17.2330(5),	14.1844(5),	17.8625(13),
	36.4215(11)	16.5269(6)	19.9467(14)
α, β, γ (°)	90, 90, 90	88.934(2),	90, 92.537(4), 90
		67.871(2),	
		70.387(2)	
V (Å ³)	6168.7(3)	2552.63(17)	3496.6(4)
Ζ	8	1	4
ho (mg m ⁻³)	1.690	1.537	1.658
$\mu (mm^{-1})$	1.758	1.099	1.566
F (000)	3144	1202	1756
Crystal size (mm)	$0.06 \times 0.07 \times 0.52$	$0.23 \times 0.32 \times 0.44$	0.10 imes 0.10 imes 0.55
Temperature (K)	291	200	200
heta (min–max) (°)	2.2, 28.3	1.8, 28.4	1.0, 28.5
Data set	–13:13; –21:23; –39:48	-16:16; -18:18; -22:22	-13:13; -15:23; -24:26
Tot., unique data, R _{int}	59227, 7697, 0.057	89900, 12681, 0.022	47673, 8764, 0.049
Observed data $[l > 2\sigma(l)]$	5439	11724	7719
N _{reflections} , N _{parameters}	7697, 434	12681, 748	87.64, 459
$R [F^2 > 2\sigma(F^2)], wR(F^2), S$	0.0457, 0.0849, 1.11	0.0237, 0.0615, 1.05	0.0907, 0.1849, 1.28
Δho_{min} , Δho_{max} (e Å ⁻³)	-1.72, 0.67	–0.78, 1.54	-3.18, 2.10

Table 6. Crystal and structure refinement data for 1–3.

Intramolecular hydrogen bonding in **1–3** is facilitated by migration of the phenolic proton to the azomethine nitrogen, resulting in an electron-rich phenolate anion. These interactions are present in the form of a keto-imine (N1–H1…O11) with an average donor to acceptor bond length of 2.596 Å (for **1**), 2.661 Å (for **2**) and 2.659 Å (for **3**) (Table 5). The hydrogen bonding networks for the three complexes are displayed in Figures 9(a–c). The crystal packing of **2** and **3** also revealed intermolecular interactions between the azomethine nitrogen and the nitrate, and from the nitrate oxygen and the uncoordinated methanol oxygen. Additionally, weak C – H…O contacts between the nitrate and phenolate oxygens participate in the stabilization of the crystal lattice. The crystal and structure refinement data are presented in Table 6.

3.7. Cyclic voltammetry

The electrochemical behavior of **1–3** referenced against Ag/Ag^+ (in 10^{-3} M DMF) at a scan rate of 150 mV/s is presented in Figure 10. The two peaks detected at –0.514 and –1.867 V (for **1**), –0.176 and –1.383 V (for **2**), and 0.5 and –2.001 V (for **3**) are assigned to ligand-based reduction of the imino and phenolic groups in HL_{1–3}, respectively [49,76]. Correspondingly, the cathodic peak potentials observed at –1.00, –0.849 and –1.00 V, respectively, for **1–3** are attributed to reduction of Nd(III) to Nd(II). The anodic peak potentials are detected at 1.64 V (for **1**), 1.56 V (for **2**) and 1.64 V (for **3**), which suggest that the Nd(III)/Nd(II) electrochemical reaction is reversible [77].

The trends observed in the $E_{1/2}$ values of **1–3** are highly impacted by the nature of the ligand in relation to the metal ion. The electron-rich ligand exhibits ease of reduction, leading to a more positive cathodic potential. This is supported by the more



Figure 10. Cyclic voltammographs of the 10^{-3} M DMF solutions of 1–3.

negative reduction potential of the *meta*-OCH₃ substituted ligands (**1** and **3**), compared to the *para*-OCH₃ in **2** which is reduced at lower energy. Furthermore, the addition of an electron-withdrawing substituent decreases the electron density of the aromatic ring of the ligand. This effect is depicted by the "higher" reduction potentials observed in HL₃ as a result of the additional electron-withdrawing –OCH₃ substituent on the second benzene ring. Complexes **1** and **3** exhibit similar electrochemical behavior, which is related to the similar coordination modes. The study illustrates the impact of the ligand substituent position on the redox properties of the lanthanide complexes, which can be modified to yield the desired redox behavior [78,79].

4. Conclusion

In this study, the addition or removal of ligand substituent on Schiff bases of the [(phenylimino)methyl]phenol-type was investigated in order to understand the effects of changes in the ligand environment on Nd(III) complexes. The slightest modification to the ligand structure has the potential to introduce or enhance the applications of these compounds [80,81].

The reaction between $[Nd(NO_3)_3 \cdot 6H_2O]$ and the *o*-vanillin-derived Schiff base ligands HL_1 , HL_2 and HL_3 yielded mononuclear complexes described by the formulas $[Nd(HLx)_2(NO_3)_3]$ where x = 2 (1) and 4 (3), and $[Nd(HL_2)_3(NO_3)_3]$ (2). The influence of the ligand environment on the bond parameters, the stereochemistry and the electrochemistry of the lanthanide compounds was demonstrated using *physicochemical* techniques.

The azomethine group did not coordinate; instead, the phenolic proton migrated to the azomethine nitrogen to form a zwitterion. The Schiff base ligands coordinated bidentately to Nd(III) *via* the phenolate and the methoxy oxygens in **1** and **3**, and monodentately through the phenolate anion for **2**. The data revealed the shorter bond lengths observed for Nd–O_{phenolate} when compared with Nd–O_{methoxide} are a result of the more electron-rich phenolate oxygen consequent to proton migration.

20 👄 S. PIKOLI ET AL.

SHAPE analyses of the three compounds revealed the sphenocorona (for 1), muffin (for 2) and tetradecahedron (for 3) geometries.

The inclusion of a second methoxy substituent in HL_3 caused a decrease in the reactivity of the conjugated system, indicating that the $-OCH_3$ moiety is electron-withdrawing, which leads to weaker interactions with Nd(III). In all three complexes the nitrate ion remains bonded in a bidentate manner to the metal ion. The influence of the ligand substituent is also illustrated in the fluorescence studies where the addition of a methoxy substituent causes weaker interactions with the neodymium ion, resulting in less energy transfer. However, HL_1 efficiently transferred energy to Nd(III) ion, resulting in $4f \rightarrow 4f$ centered emissions. The redox properties reveal an electron-rich environment will be reduced at more positive potentials.

Acknowledgements

Instrumental facilities provided by the Nelson Mandela University and Stellenbosch University are gratefully acknowledged.

Funding

This research was supported by the NRF [NRF Grant No. 106004] and the Nelson Mandela University Postgraduate Research Scholarship (PGRS).

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22 🕢 S. PIKOLI ET AL.

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